Synopsis on

"Resource Recovery and Reduction of Waste through Clean Technology Options "

August,2020

Submitted for registration in the degree of Doctor of Philosophy

DEPARTMENT OF CIVIL ENGINEERING

CHITKARA UNIVERSITY

HIMACHAL PRADESH

Submitted by

Avinash Kumar Sharda (PHDENG-18053)
Under the joint supervision of

Dr Varinder S Kanwar
Vice Chanceller, Chitkara University
Himachal Pradesh

Dr Ashok Sharma
Cleantech InternationalFoundation
Chandigarh

Table of Contents

S. No	Section	Page No.
1	Introduction	3
2	Literature Review	3-13
3	Research Gaps	13-18
4	Need of Research	18-20
5	Scope of Research and Research Challenges	20-21
6	Objectives of the Study	21
7.	Research Methodology	22-24
8.	Data Collection and Analysis	24
9.	Time Schedule	25
10.	References	25-27
11	Abbreviation Used	27
	Annexure 1-A	28
	Annexure 1-B	29

1. Introduction:-

Effluent Treatment and Solid Waste Management scientifically is a big challenge in process industries because of it is in enormous quantity, complexity and hazardous in nature. Due to enforcement of stricter environmental regulations, it has resulted into a very sedative approach by industry in implementation of effective treatment technology. It has further aggravated the situation in developing countries facing challenges of rising population, increasing urbanization and industrialization. The purpose of the this research study is to review existing practices in the process industries like Textile Dyeing, Food and Herbal, Pharmaceuticals(API) and FMCG by implementing cleaner technologies besides introducing advance techniques at source and in the end of pipe treatment.

These processing industries across the globe generate huge quantities of wastes and proper management of these wastes is an uphill task . A big problem frequently encountered in these process industries is waste water, emissions and solid waste are highly variable in nature as composition of the raw materials vary widely for one class of products to another. Many processing industries use pretense to confidentiality of composition so that they can escape from regulations of stringent pollution control norms. Generalization in treatment approach in such cases turns difficult because of poor empirical relation between raw material consumption and operational parameters like BOD, COD, TSS, TP and Oil which further complicates the treatment process.

Under this perplexing situation, revisiting the existing treatment technologies and prevalent practices of handling process industry waste water, residues and other solid waste is absolutely necessary so as to come out with clear suggestions towards formulation of best strategies and directing research for developing sustainable technologies.

2. Literature Review:-

The literature of the in process and end of pipe initiatives were reviewed after detailed study of the research articles published in the national and international journals of high repute. By acknowledging references relevant with the topic of the research, gaps in the past research, gave the scope for our study. The various studies incorporated in research articles reviewed in tabulated form are as under:-

Year of Publication	Authors	Title	Source	Summary
2011	Parveen Kumar et.al	Advance Oxidation of Pulp and Paper Industry Effluent	International Conference on Environmental and Agricultural Engineering	The advanced photo catalytic experiments were performed with UV/TiO_2 and UV/TiO_2/H_2O_2. Addition of H_2O_2[1] enhances removal of organic matter of Primary clarified effluent by 57.9% in COD ,42.9% in BOD and 89.2% in color and of bio-treated effluent 74.8% in COD ,52.7% in BOD and 95.4% respectively and complete degradation of chlorinated organics and effluent was diluted to bring critical values around 500mg/l[2]
2013	Noemi et,al	Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry	Elsevier	The advanced Oxidation Processes (Ozonation and TiO_2) coupled with Biological Treatment were MBR[3] studied for effluents of recycled paper mill and a Kraft Paper Mill and Ozonation achieved about 35% COD reductions for effluents from a recycled paper mill and about 60% for the effluent sampled for Kraft paper Mill. Although several authors have reported a higher effectiveness of Ozone treatment at basic pH values because of formation of OH radicals[4][5]
2006	Pantelis et.,al	Treatment of textile dye house waste water by TiO_2 photo-catalysis	Elsevier	The UV-A induced photo catalytic oxidation over TiO_2 suspensions for different duration of treatment, concentration of TiO_2 and at varying pH values. Two crystalline forms of TiO_2 viz. anatase and rutile were tested. It was observed that with increase of TiO_2 concentration of up by 0.5g/L, above which the degradation COD remain constant at value of 40%,however discoloration was found to be almost 100% at pH values of 6.7. Different behavior was observed at pH value of 3 where discoloration and COD reduction was found to be 100% and 92% respectively.
2016	Rajindiran	Photo	IARJSET	Discoloration and Degradation study

	.S et.al	catalytic – Ozonation of Textile Dyeing Waste water using Fixed Catalyst System		of six real textile dyeing waste waters were experimented using fixed catalysts mode photo catalytic –ozonation ($UV/TiO_2/O_3$) processes yielded complete color removal with 64% COD removal after 30 minute of treatment
2007	Abbas J. Attia et.al	Photo catalytic Degradation of Textile Dyeing Waste water Using Titanium Dioxide and Zinc Oxide	E.J. Chem	Photo catalytic Degradation of textile dyeing waste water using TiO_2 and ZnO was conducted under ultraviolet irradiation followed by measurement of absorbance of ʎmax 380nm. Maximum color removals were observed as 96% and 82% using TiO_2 and ZnO respectively
2018	Palle Lindgaard et.al	Road Map towards Zero Water Milk Processing Plants	Macro think Institute	The study was conducted for preparing road map towards Zero Water Milk Processing Plants. Developed a documentation program me with list of data to be collected by the plants as (water supply, waste water generation ,chemicals used and labor time). Water to Milk ratios for different milk processing plants manufacturing products like milk products, Yellow hard cheese, white cheese and Mozzarella cheese has been reported as 1.29,1.36,1.84,0.68 and 0.88 and waste water to milk ratios has been reported as 1.35,0.83,1.30,1.54 and 0.79 respectively. The COD in waste water ranges from 1800-4000mg/l equivalent to loss of product 139-839 tons of milk proteins annually. Smart metering,data integration ,up-gradation of CIP processes ,recycling of RO treated effluents into processes and reuse of MBR treated in cooling condenser in different milk processing plants resulted in water savings up to 200,000m^3-250000m^3 per year which is 15% of total water use of 1600,000m^3 by regulated water use mapping[7] and

				[8]
2014	Coskun Aydiner et.al	Techno-economic viability of innovative membrane systems in water and mass recovery from diary waste water	Elsevier	Techno economic analysis of whey concentration for recovery of powder and water using FO/MD and MD/RO. Raw whey was concentrated to solid content of 21% and 25% respectively [9]. To carry out the studies different RO/FO flat sheets and MD membrane sheets made of polypropylene(PP) and poly-venyldentlorid (PVDF) having 0.22 pore size were selected. The estimated simulated performances in MD/FO,MD(PVDF)/RO and MD(PP)/RO has been reported as 67.3%,65.6% and 67.6% respectively which is 2.2-2.3 times greater than UF/RO(29.8%).In case of FO/MD integrated systems effective concentration of cheese whey can be provided despite high Chloride content and COD concentration in the influent , however very low values of 12.0mg/l and 38.0mg/l has been measured in the effluent respectively. Simulated design for $100m^3$/day showed that water can be recovered in sufficient quantity to be reused in cheese production . The economic performance of both FO/MD and MD/RO were determined as good as UF/RO used widely in process compared to others. Besides both systems yielded a return of 12-13million $ with annual profit of 800,000 $ as compared to UF/RO. Pay back periods of the system investments were determined satisfactorily as under 1 year due to annual revenues 3.4 million $ from water recovery and whey powder selling. An attempt to treat effluent from cheese whey by hydrogen production and photo fermentation with two stage reactor) Rhodo pseudomonas palustris (with two stage reactor)[10]

2012	Ana R.Prazeres et.al	Cheese Whey Management : A review	Elsevier	Review study was conducted to analyze different solutions considering it as an effluent with nutrition value ,strong organic acid and saline content . Focused further on developing biological treatment with and without valorization, physicochemical treatments and land application. Cheese whey a green yellowish liquid resulting from the precipitation and removal of milk casein in cheese making process[11]. The riboflavin (vitamin-B2) resulted in yellow colour of the whey[12]. Milk lactose contributes around 39-60kg/m^3 constituting around 90% of the organic load[13]. Fats and Proteins partially responsible for organic contaminants with values ranges from 0.99-10.58kg/m^3 and 1.4-8.0kg/m^3 respectively. BOD and COD values have been reported as 27-60 kg/m^3 and 50-102 kg/m^3 respectively. BOD_5/COD ratios higher than 0.5 indicating that substrate is treatable biologically. Inorganic contamination is due to addition of NaCl during cheese production can cause problems in operation of biological digestors Cheese whey treatment through valorization is common technique since it contains about 50g of lactose and 10g of proteins further exceeded for production of powdered products. Hydrolysis of lactose and proteins is another option for generation of lactose monosaccharide's (Glucose and glactose),peptides and amino acids. The another option is application of physicochemical treatments followed by aerobic and anaerobic treatment . The residual COD concentrations for JIMBR (Jet

				Loop Membrane Bioreactors) and Activated sludge process has been reported as 5.8 kg/m^3 and 10.7-24.0kg/m^3respectively.The cheese whey anaerobic biotransformation is active under mesophillic condition (35-37^{0}C)[16] further claimed that USAB is a very efficient reactor when dealing with diluted CW showing 95-97% COD removals. Fermentation of CW to produce ethanol was an another option[17] . Degradation of VFA by methogenic bacteria is lower than production by acidogenic bacteria. The low carbonate concentration avoids its buffering effect and subsequent acidification besides polymerization of lactose with formation of oligosaccharides The alcoholic fermentation of lactose from Cheese Whey is hardly economical competitive if compared to other substrates such as cane sugar, corn starch and lingo cellulosic biomass etc. Electrochemical coagulation with iron electrodes has been tested for treatment of cheese whey effluent with initial COD of 27.6kg/m^3[21] achieving a COD removal of roughly 53% and clarified supernatant presented a residual COD 13kg/m^3. Cheese whey recovery around 73.8% has also been reported by applying electrochemical coagulation[22].The other processes like ultra filtration (UF), Nano Filtration(NF) and Reverse Osmosis(RO)[23] have been widely reported with protein retentions in the ranges of 56-81,87-100 and 94-96% respectively. Few studies have reported the treatment of permeates and the majority of the works apply a fermentation post treatment to the

				produce ethanol , hydrogen or lactic acid. Thus effluents coming from micro and ultra filtration stages still show a considerable residual COD values in the proximity of 54kg/m^3 and a phosphate content of 0.800 kg/m^3. Permeates coming from Nano filtration and reverse osmosis present lower values of COD values with in range 1-30 kg/m^3 depending upon operating conditions. The high values of COD in microfiltration and ultra filtration effluents are due to the lactose content (10%). Additionally, the ultra filtration permeate has a BOD_5 value of 30-45 kg/m^3 [24].The high bio degradability (BOD_5/COD=0.5-0.8) of the ultra filtration makes viable application of biological treatment
2011	C.B Cota-Navarro et.al.,2011	Hydrogen and methane production in two stage processes using mixed cultures and cheese whey powder	Elseveir	Resource recovery study conducted for Hydrogen production from the inoculums was prepared from anaerobic granular sludge from a full scale UASB reactor in confectionary factory and methane production from anaerobic granular sludge from UASB in Pulp and Paper industry. In case of continuous –flow stirred tank reactor (CSTR) cheese whey powder with soluble lactose content of 79% and 12% protein was supplemented with different minerals for hydrogen production and further reported Hydrogen production rate of 28 LH_2/L/d obtained during stable operation at HRT and OLR of 6h and 142g lactose /L/d respectively. Regarding methane production in USBR , the acidified effluent from the hydrogen producing bio-reactor was efficiently treated obtaining COD removals above 90% and OLR and HRT of 20g COD/L/d and 6h respectively. effluent from hydrogen

				producing bioreactor. Hydrogen production reactor was operated for 48days in same period under different OLR and HRT and during whole process , the hydrogen content in the gas phase was between 50-54%(v/v) with only CO_2 as secondary component ,methane was not detected[25].
2010	Jai Parkash Kushwaha et.al	Organics removal from dairy waste water by electro chemical treatment and residue disposal	Elsevier	Prepared simulated dairy waste water by dissolving 4g of milk powder per liter of distilled water with the main characteristics were COD-3900mg/l, Total Solids -3090 mg/l, turbudity-1744 NTU, conductivity -220 us/cm, chloride -31mg/l and total nitrogen (TN)-113.18 mg/l and pH- 6.3-6.8. Operational parameters such as current density(J), dosage of NaCl (m), electrolysis time(t) and pH-6.3-6.8 were varied between 61.73-308.64A/m^2,0.2g/l,10-90 minutes and pH 5-11 respectively. For value of m=0 , the optimum values of J,m,t and pH were found 270A/m^2,50min and 7.0 respectively. According to response surface methodology (RSM) has successfully employed in EC treatment of SDW using iron electrodes .COD,TS,TN and turbidity removal efficiencies have been reported as 70%,48.2%,92.75%and 99.8% respectively. The cost of both electricity and electrode consumption required to run the system at optimum conditions to reduce COD of 1 m^3 diary waste water from 0.43kg/m^3 to 0.43-15.2 kg/m*3* to 0.129-4,6 kg/m^3 is in the range of 0.72-2.55 $. The disposal study by TGA/DTA analysis showed that generated sludge and scum can be used as fuel in the boilers and incinerators or can be used for production of fuel briquettes
2008	Chia-Yuan	Pharma ceutical	Elsevier	Selected 20 m^3 capacity tanks for

	Chang et.al	waste water treatment by membrane bioreactor process-a case study in southern Taiwan		treatment of pharmaceutical waste water by Membrane Bioreactor(MBR). First tank of 10 m^3 capacity tank with diffused aeration tank for biological treatment and second tank with duel function of biological treatment with solid - liquid separation by providing hollow membrane made of PVDF. The regulation requires the COD levels below 450mg/l in order to discharge into tertiary treatment plant which has an effluent COD limit of 50mg/l. After 30 days od seeding and start-up, the MBR plant was monitored continuously for 140 days . COD and BOD reductions have been reported as 96% and 99% respectively with F:M ratios of membrane tank(kg COD $MLVSS^{-1}d^{-1}$) range between 0.003-0.079. The MLSS concentration was maintained in the range of 6000-17000mg/l with average SRT>40days.
2000	Qingyong Lang et.al	Super fluid extraction in herbal in herbal and natural product studies- a practical review	Elsevier	SFE is widely accepted in recent years as an alternative to conventional solvent extraction methods for separation of organic compound in many analytical and industrial processes[26]. SFE (Super Fluid Extraction) as an environmentally responsible and efficient extraction technique for solid material was introduced and extensively further studied for separation of active compounds from herbs and other plants. SFE uses no or significantly less environmentally hostile organic solvents. The supercritical CO_2 has good solvent properties for extraction of non polar compounds such as alcohols, esters, aldehydes and ketones. It has been further reported that modifiers play a very important role to obtain desired polarity of CO_2 based fluids . By

				selecting modifiers one can readily manipulate the properties of fluid .
2000	Pathumthip Tonthubthi mthong et.al	Supercritical CO_2 extraction of nimbin from neem seeds – an experimental study	Elsevier	Experimental study for extraction of nimbin from neem seeds using CO_2 as superficial fluid extraction. Extraction carried out at in the range of operating pressures from 10 to 25 MPa, temperature from 308 to 333K and flow rate varied between 0,24 to 1.24 ml/min. It was observed that optimum extraction was observed at 23 MPs and temperature of 308 K and flow rate of 1.24 ml/min for neem sample of 2g. Best extraction were measured rate was found to be 0.18mg of nimbin/g neem seed per hour of operation which is equivalent to 0.35 kg nimbin present in 1 kg of neem seeds. In addition to above CO_2 has been observed as an inert, nonflammable, non explosive, inexpensive ,odorless and clean solvent which leaves no residues
2018	Andras Jozsef Toth et.al	COD reduction of process waste water with vacuum evaporation	Journal of Waste Treatment and Recovery	The study was conducted on COD reduction of process waste water with the vacuum evaporation of Process Waste Water(PWW) from chemical industry. The heat pump vacuum evaporator was evaluated in order to reduce the chemical oxygen demand[28] from initial 7500mg O_2/l to the lower value below the effluent limit , which is 1000 mg O_2/l. Experiments are investigated with the LED Italia R150-v3 pilot apparatus. It has been further reported that evaporation rates are influenced by operating pressures between 40 and 50 mbar. The highest yield can be achieved at 40 mbar, where boiling point is 32.8^{O} C. The chemical oxygen demand is also the lowest using 40 mbar.
2018	Mehrdad Ahmadi et.al	Effect of Nanobubble aeration in oxygen	JAEHR	Effects of Nano bubble aeration in oxygen transfer efficiency and sludge production in waste

		transfer efficiency and sludge production in waste water biological treatment		biological treatment" was studied and it was reported that compared to micro bubble aeration , nano bubble aeration increased the concentration of dissolved oxygen in the mixed liquor of the reactor (from 2 to 4.5 mg/l), while reducing the production of excess sludge from 100 to 40 ml/g (SRT: 15-40 days). With the same SRT duration , these values were within the range of 160-70ml/g using fine bubble aeration . According to results , nano bubble aeration could increase the efficiency of aeration , thereby increasing the efficiency of aeration , thereby increasing the capacity of treatment plant and reducing the cost of biological waste water treatment

3. Research Gaps:-

The literature studies carried out by the various authors gives a perspective approach in technical evaluation of pollution prevention through cleaner productions, induction of in process innovations, implementation of advance treatment technologies in the end of pipe treatment and higher profitability through improved process efficiencies. Accordingly the following research gaps have been identified in view of issues correlated to process industries located in the study area selected the following gaps are visualized-

- The studies conducted earlier were limited to experimentation at pilot scale without any further implementation at industry level. The techno economic evaluation of these studies are limited and in most of the cases without assessment of pay back periods.
- The focus was mainly limited for implementation of low cost end of pipe treatment without evaluating techno-economic feasibility for recycling of treated effluent unto process after implementation of BAT (Best available technologies)
- Lack of finding attractive innovations through induction in process techniques and intensification measures.
- Unsatisfactory outcome through by product recovery, reduced energy consumptions (Thermal as well as electrical) and reduced waste water generation and water consumptions.
- End of pipe initiatives are mainly to ensure compliance to the discharge and emissions standards instead of introducing advance treatment technologies.

- Limited cleaner production options through source segregation of streams based on pollution low and high pollution loads. Which could further lead to recycling and resource recovery.
- Lacking skills in getting water audit through reputed technical institutions implementing concept of water mapping, water saving and reuse scenario by prioritizing 6Rs approach i.e. Reduce, Renew, Reuse, Recycle, Reclaim and Return water. As per literature reviewed the details of gaps observed are tabulated as below:-

Author's Name	Gaps identified
Parveen Kumar et.al.: 2011.	1 As reported in the study that biological treatment is in efficient for the removal of the color, and complete degradation of chlorinated organics and effluent was diluted to bring critical values of COD around 500 mg/l[2] before the photo catalytic degradation with optimized conditions, which would have limited effect in overall treatment for reduction of COD and BOD. 2 As the study has been carried out on pilot scale no techno economic evaluation has been carried out in case of implementation of study in full scale. 3 Apart from advanced oxidation processes no other intensification measures to improve oxygenation in the aeration tank have been recommended in the biological treatment.
NoemiMaryo et.al. : 2013	It has been reported that ozonation and photo catalysts have not been usually considered as feasible treatments to be used stand alone, because large amount of chemicals and energy that they require for its performance, but their combination with biological process (MBR) may increase overall efficiency, but the incorporation of these methods with the other conventional biological processes have not been included in the study
PantelisA.Pekakis et.al.; 2006	1 The COD reductions in waste waters with pH 9.8 has been reported as 40% and 55% at TiO_2 concentrations of 0.25g/L and 3g/L respectively indicating that low degradation of inorganic and organic compounds in the textile waste waters shall be resulting into loadings on WWTP. The discoloration rate may be satisfactory but

	overall treatment efficiencies for reduction of toxicity and COD loadings are required to be ensured. 2 The comparative evaluation of TiO_2 with other Advance Oxidation Processes i.e. O_3, H_2O_2 /UV and TiO_2 /UV have not been included in the research , whereas same has been referenced in the study only [6]
Rajindiran.Set. al.;2016	Comparative efficiencies of different combinations i.e. O_3 with TiO_2 and UV separately has not been worked out along with the treatment costs especially when environmental penalty in the case is considered in (textile waste water , the main problem is the chloride content)
Abbas J, Attia et.al;2007	In the study the focus was mainly on discoloration achieved up to 96% by TiO_2 and 82% by using ZnO at 303K based on photo catalytic degradation , however COD reductions has not been reported besides level of biodegradability. Also COD/BOD ratios have not been reported besides cost evaluation for choosing best treatment method
Palle Lindgaurd et al;2018	Only parameter COD measured with its range over all the milk processing plants where as individual values plant wise has not been reported. In addition to this other biological parameters i.e. BOD, pH, Proteins, Lactose, Turbidity, Alkalinity and Fats have not been analyzed and reported
CoskunAydiner et.al;2014	Although economic feasibilities of the final combined systems were being carried out using process design software equipped with cost estimation module (Intelligent Super Pro Designer)V 7.5) by calculating material balances of three membrane systems at a design in flow of 100m^3 per day in initial step of economic analysis only membrane cleaningwas frequency was taken into account in terms of application into the practice. The design membrane fluxes were 4.0/4.0l/m^2h and 7.3/40.0l/m^2.h for FO/MD and MD/RO systems respectively along with 10.3/33.4/40.0l/m^2.h for UF/RO. In all the systems membrane cleaning costs have been neglected in the economic analysis of the systems, which is important component for recovery of water and whey powder.
Ana R. Prazeres	1 As reported in the study that cheese whey effluent is rich in nutrients, proteins, lactose ,minerals and lactic acids which

et.al;2012	are treatable and recoverable through advance treatment and in process technologies , however the organic contamination of cheese whey is attributable to the mineral salts present (0.46-10%), principally NaCl and KCl (>50%) and calcium salts (primarily phosphates)[14] . Inorganic contamination is consequence of addition of Na Cl during cheese production. High sodium content can cause problems when operating biological digesters [15]. Acidic pH (3.5-6.5) and low alkalinity also affect the biological treatment efficiency. The study has not included the evaluation of cost associated studies for the management of cheese whey. 2 In general the anaerobic digestion presents a high organic removal efficiencies , however , the values of alkalinity (bicarbonate) about 50 meq L- can lead to failure of anaerobic digesters . Since the degradation of rate of generated volatile fatty acids (VFA) by the methanogenic bacteria is lower than their production by acidogenic bacteria VFA's rapidly accumulate in the medium. The low carbonate concentration avoids its buffering effect and subsequent acidification of the reaction medium occurs [18]. As a result the anaerobic treatment presents a great difficulties at the time of maintaining stable operation. 3 In case of lactose enzymatic hydrolysis results into polymerization of lactose or glucose with the formation oligosaccharides[19] and lactose mass transfer of cells formation is limited. 4The bio-conversion of lactose and to ethanol reveals a theoretical maximum value of 0.538 kg of ethanol per kg of lactose consumed . The alcoholic fermentation of lactose from cheese whey or whey permeates is hardly economical competitive if compared to other substrates such as cane sugar, corn starch and lingo cellulosic biomass etc. [20]. In general production of ethanol a with lactose/sugars concentrations between 35-50 kg/m^3 is not economically feasible. Also the substrate consumption efficiencies ranges from 70-100% the ethanol concentration is rather low (2.1-20 kg/m^3) and effluent shows a considerable residual COD (15kg/m^3), a better odor is experienced .

C.B Cota-Navarro et.al; 2011	No satisfactory results were obtained with 13 L/L/d was produced at HRT as low as 3to5h and OLR of 163g lactose/L/d respectively as the operation was not found stable at these operating conditions. The study was conducted at laboratory scale, however the field application with outcome of results in view of implementation of the results has not been incorporated, besides evaluating techno economic feasibility.
JaiParkash Kushwahaetal; 2010	The recommendations regarding use of residues and scum as a fuel in the boilers/incinerators, although have been specified with optimum calorific values of sludge and scum as 17.72 MJ/kg and 18.73MJ/kg respectively, but the impact of emissions after combustion on the air quality has not been incorporated in the study.
Chia-Yuan Chang et al; 2008	1.Fouling on membranes outer surface has been reported due to micro-organism and physiological properties of the sludge are required to be replaced thus increasing cost of treatment. 2. As reported in the study relationship between MLSS and Viscosity increased logarithmically as the concentration of MLSS increased and variation is different from other studies implying that further study could be carried out.
Quingyong Lang etal., 2001	1. The review article covers theoretical aspect with main focus on advantages of SEF technique, Fluid materials and modifiers, Conditions for extraction , collection and online fractionalization and coupling with chromatic methods and has not referenced any case study with operating conditions such as CO_2 Flow rate, CO_2 pressure, extractor temperature and weight of sample. The model for carrying out research study has also not been reported. As per literature review [27] conducted study on Supercritical CO_2 extraction of nimbin seeds. Nimbin is one of the many substances found in neem seeds and is reported to have several medicinal properties and uses. 2 The application of SFE on allopathic pharmaceutical products has also not been reported in the review article
PathumthipTonthebtthimthong et;al:2001	1 Cost evaluation in the study has not been carried out as the cost factor is an important indicator for choosing the best treatment method besides the stage where the said research to be implemented

	has not been mentioned. 2 The size of the sample taken was limited and nimbin being a medical substance and use of a co-solvent in extraction process might affect the medicinal properties of extracted nimbin and might hinder future FDA approvals.
AndrasJojsefToth et.al. :2018	1. Since maintenance of heat exchangers is a crucial exercise . Encrustations , fouling and corrosion disturb the heat transfer to liquid and decrease the energy efficiency. No data on the concentration of contaminants ,or surrogate parameters (TOC, pH, conductivity, etc.) has not been reported which are the most important monitoring parameters as for as operation of evaporators are concerned besides preventing condensate transfer to the pollutants
Mehrdad Ahmadi et.al. :2018	The pilot study conducted was limited to SBR Sequential Batch Reactor , however no data and reference regarding comparison to other conventional activated sludge process systems have been covered. Moreover details regarding nano bubble generator has not been reported in the study.

4. Need of the Research:-

The various process industries such as textile dyeing, pulp & paper manufacturing, food processing, herbal extraction and pharmaceuticals (API) etc. have been established in Himachal Pradesh in the past 15-20 years and has enhanced their production capacities post excise package by central government in 2003. The major growth of these process industries has also taken place in the lower Shiwalik mountain ranges adjoining to border states of Punjab, Haryana and Uttrakhand. It is pertinent to mention here that aforementioned industrial sectors are the locomotive for developing countries like India and the study areas selected are justified for carrying out research which can further be extended for implementing case study in neighboring states also.

Accordingly case studies of following sectors were selected to carry out process audit, water balance, energy balance and material balance.

- Pulp and Paper Manufacturing
- Food Processing and Diary Industries
- Herbal Extraction and Pharmaceuticals (API) drugs manufacturing units.

In view of literature review the issues reported by various authors in their respective articles indicate that the wastes from aforementioned process industries continue to pose big treatment challenge largely because of adoption of wrong or faulty approaches. The sector wise issues are detailed as below:-

Pulp and Paper Industries effluents contain a variety of toxic organic compounds and are major source of industrial pollution world wide . The pulping and bleaching steps generate most of liquid, solid and gaseous wastes. High content of organic matter ,which contributes to Biological Oxygen Demand(BOD) and depletion of dissolved oxygen in the receiving ecosystems. In pulp and paper sector the agro-residue mills typically employ a soda or alkaline sulfite pulping process and most of the lignin present in the black liquor is the high-molecular –weight fraction, a key factor contributing to low BOD/COD ratio. Pollution reduction through plant process modification and advanced oxidation of pulp and paper industry of effluents can be resulted into reduction of pollution load. The bio pulping method utilizes whole cells of micro-organisms and microbial enzymes. However further research is required to optimize the conditions required for enzymatic pulping of herbaceous fiber and commercialization of the process besides replacement of elemental chlorine with liquid oxygen, ozone, caustic soda and H_2O_2. In the end pipe of treatment photo-oxidation and Fenton's reactions involving H_2O_2 and ferrous ions shall be an effective option. The increase in mass oxygen transfer through advanced aeration equipments shall also increase DO concentration and reduced BOD loads in the aeration tanks.

The **Diary Industries** are associated with generation of large volumes of waste water and this waste water contains milk and milk products with wash water. Also the diary processing effluents are ranked among the major sources of industrial water pollution. In diary waste water biological oxygen demand (BOD),chemical oxygen demand (COD) and nutrients levels are very high. These waste waters can cause environmental damaged if discharged without treating. The waste water containing whey is subjected to recovery of water using advance technologies besides raw whey was concentrated to produce commercial by product. The injection of electro coagulation (EC), Fenton's reaction and ozone processing can be applied in treatment of diary waste water. Water use mapping and water saving and reuse can be documented after application of aforesaid technologies

Replacement of traditional solvents with CO2 extraction is receiving increased attention in **Herbal extraction and API drugs manufacturing units .**Due to enforcement of stricter environmental legislations , supercritical fluid extraction(SFE) has gained wide acceptance in recent years as an alternative to conventional extraction for separation of organic compounds. A substance is termed as supercritical when its pressure and temperature are greater than its critical pressure and critical temperature . For Herbal extraction and pharmaceutical applications CO_2 is an ideal processing medium. Furthermore carbon dioxide is nontoxic , non flame able , relatively inexpensive , recyclable and generally regarded as safe. Of all the gases and liquids studied , CO2 remains the most commonly used fluid for SFE applications because of low critical constants(Tc=31.1^{o}C:Pc 72.8 atm), its non toxic and non flame able properties. The advance end pipe of treatment options can be supplemented such as MBR, Ozonation and nanobubble injection to aforementioned extraction techniques.

5.Scope of Research and Challenges:-

Since these sectors consume lot of water, energy, steam and chemicals. Due to excessive usage of these sources these industries produce various types of wastes including waste water, solid wastes, gaseous and heat emissions having impact on the ecology of the area. Which has resulted ecological sensitivity index i.e. CEPI (Comprehensive Environmental Pollution Index) in these industrial belts like Baddi, Parwanoo and Kala Amb reaching at alarming stage and has been categorized as severely polluted areas as per their respective index values, which has further resulted into intervention of Hon'ble courts including National Green Tribunal apart from enforcement Environmental Legislations.

The following issues justifies our research;

(a) These sectors consume lot of water, energy, steam and chemicals. Due to excessive usage of these sources, above mentioned industries produce various types of wastes including waste water, solid wastes, gaseous and heat emissions. So pollution prevention and control through introducing cleaner technologies at process stage and implementation of best available technologies at the end pipe treatment is the utmost requirement of the time for efficient use of natural sources.

(b) These shall also be helpful in implementation of technologies for reduction of pollutants in a facility through changes in product design, process technology and clean technology potential. It is directly proportional to cost of material, toxicity of materials, hazardous potential, volume of wastes and

energy intensification of process. In addition to this the study shall be helpful for future implication of Zero Impact Manufacturing Initiative (ZIMI) , which is emerging as most effective tool for carbon emission reduction globally.

(c) The wastes from aforementioned industries continue to pose big treatment challenge largely because of adoption of wrong or faulty approaches as revealed from the field visits and quite few studies [Larsson et.al (2007), Zuccato et.al (2005)]. Amidst such wrong approaches, irresponsible and indiscriminate release of wastes into water bodies leaves potential risk of adding to levels of pollution through BOD and COD loadings and other toxic substances. By adopting cleaner technologies at process levels in these process industries for the reasons mentioned above and advance treatment technologies may resulted into decrease in pollution loads besides energy recovery, reduction in waste water generation. The payback period of this clean technology may be limited in the range of 1 to 2 years.

6.Objectives of the Study:-

The case studies of different process industries mentioned above also propagates road map towards water conservation and minimum waste water generation with the objective of work

- To apply in process technical innovations to recover by products in order to achieve higher productivity, good economic benefits and advance treatment technologies in the end pipe of treatment to water reuse and energy conservation in all the selected process industries.
- To formulate methodology for achieving approach (6R's) i.e. Reduce, Renew, Reuse, Recycle, Reclaim, and Return through road map towards Zero Water Diary processing industries.
- Application of clean technology in processes for source reduction of pollutants through changes in the product design, process technology and fuel in Herbal Extraction and API Drugs manufacturing units
- The supplementation concept of ZIMI i.e.(Zero Impact Manufacturing Initiative) to advanced technologies in process and at end pipe.
- Formulation of process control systems in waste water treatment based on fuzzy logistics (continuous monitoring system).

7.Research Methodology:-

As there is enormous scope for resource recovery options in these selected processing industries , the following methodology and procedure shall be followed

- Collection of data in the selected process industries by carrying out Preliminary Audit, Process Analysis, Material Balance , Hazard/Toxicity Potential and Waste Stream Analysis besides documentation of Water to Raw Material and product ratios pre and post injection of advance technologies.
- Analytic measurement of waste water quality parameters contributing pollution load to end pipe of treatment and at the outlet to assess the efficiency of treatment by comparative evaluation pre and post injection of Advance Treatment Technologies
- Analysis of collected data by developing correlation between different parameters i.e. BOD, COD, DO, MLSS,MLVSS and Oil and Grease etc.
- Pilot scale study of CO_2 extraction at process level by introducing ozonation at CIP in Herbal and API (Activated Pharmaceutical Ingredient) manufacturing units and to evaluate effect on reduction of Pollution Load
- To study combination of ozone and electrocoagulation in process at pilot scale level for bye product recovery and MBR in the end pipe of treatment for recovery of treated waste water in diary industry
- To study and evaluate effect of advance treatment technologies measuring biodegradability index(BOD/COD) by increasing oxygenation in aerobic treatment and resource recovery through anaerobic digestion for resource recovery besides injection AOPs in Pulp and Paper industry post biological treatment for reuse of treated waste water.
- Techno-economic analysis to estimate the possible costs and benefits that would arise from real scale application in terms of reduction in costs of biological treatments , bye product recovery and low water consumptions .
- Keeping above into consideration the in process and at end pipe of treatment techniques to be applied in the selected process industries have been tabulated as below:-

Sl No	Name of Sector	Parameters to be Evaluated	Description of Advance Technologies
1	Pulp and Paper	a) Fines separation through DAF for by product recovery	Pressure driven through dissolve air separation

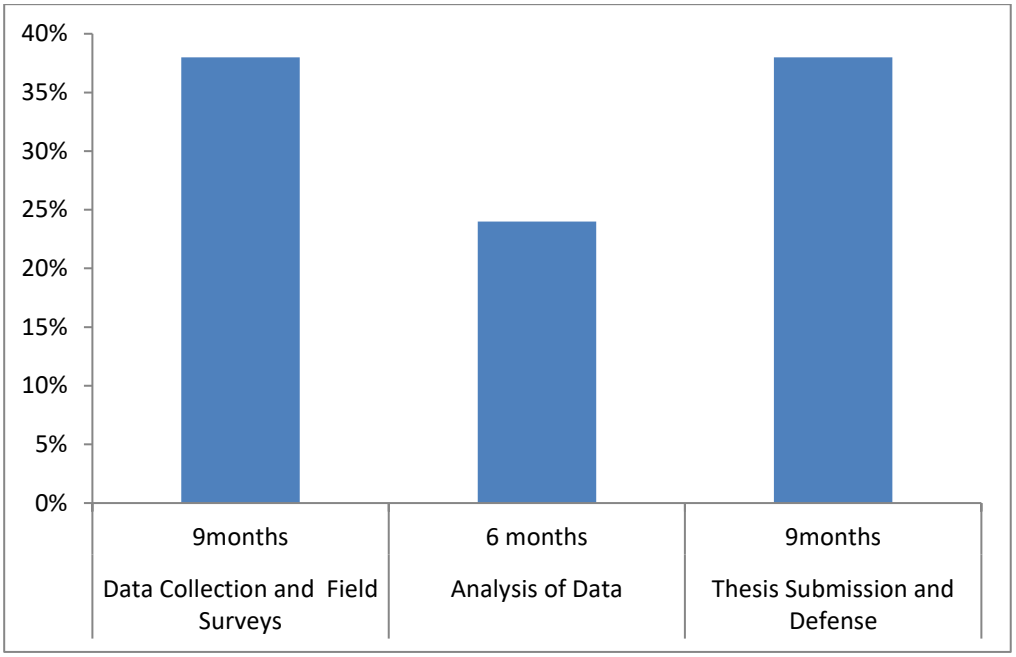
		b) Comparative evaluation parameters(DO),(BOD),(COD) and bio-degradability index(BOD/COD) ratio pre and post implementation of mass transfer oxygen intensification measures besides developing relationship between reaction constant K and sludge age Θc	By increasing aeration efficiencies of tubes-spiral roll besides provision of Jet aerators pure oxygen transfer through turbine aeration and ventoxal. Nano-bubble aeration for less energy consumption
		c) Resource Recovery by methane generation and injection of AOPs for reuse of treated waste water into process.	Anaerobic reactions such as UASB, Sequential treatment and photo catalytic oxidation with Fenton's reaction using Ferrous salts or TiO_2
2	Herbal Extraction and API Drugs Manufacturing	a) Replacement of traditional solvents toxic with "environmentally benign" substances for clean synthesis of Pharmaceutical and Herbal Extraction	A pilot scale study for using CO_2 supercritical extraction methods in API bulk drugs manufacturing and at Industrial scale in Herbal extraction process.
		b) Resource recovery option by replacement of conventional techniques with advance technology	Enhanced Diffused aeration incorporated with Membrane Bio-Reactor in aeration tank and Ozonation for improved COD and Sulphide removal at tertiary level
3	Diary Processing Industry	a)Intensification of anaerobic digestion through fermentation to ethanol and production of by product having commercial	Increase in COD removal efficiency with relatively short HRT (4 to 7 days) at Industry

		values using process modeling and cost estimation software	level study besides concentration of whey waste water through MD/RO by selection of proper membrane for low COD,TP and TN.
		b)Advance Oxidation Processes coupled with Electrochemical and incorporating advanced biological treatment in the conventional treatment	Pilot scale study using Electro coagulation process coupled with Fenton's reaction and Ozonation by measuring COD reduction at optimized current density(j), Hydrogen Peroxide (H_2O_2)/Fe_2+ and O_3 besides replacing conventional aerobic reactor with MBR
4	Miscellaneous applications	The above methodology shall be supplemented with other innovative modules Microwave Drying , Ultrasonication, process catalysts and waste heat utilization coupled with process, water and Energy Audit in all the process industries as per requirement	

8.Data Collection and Analysis:-

The formats have been devised (Annexure – 1A) and(Annexure-IB)for collection of data by conducting field visits and pilot scale studies to go through process, raw material details, energy consumptions, fuel used and end of pipe treatment solutions by induction of aforesaid initiatives in the process as well as end of pipe treatment. Further data collected shall be subjected to various regression models for optimization of control parameters with in process and at end pipe of treatment. The pollution balance equations shall be developed for minimization of waste production in the process based on generic pollution balance besides introducing a "pollution index" defined as mass of waste produced per unit mass of product. The testing facilities available at University will be used, at the same time help from HP State Pollution Control Boards Laboratories will also be taken.

9.Time Schedule:-



10. References:

[1] A. C. Rodrigues., M. Boroski., J. C. Garcia., N. S. Shimada., J. Nozaki and N. Hioka.Treatment of paper pulp andpaper mill wastewater by coagulation-flocculation followed by heterogeneous photocatalysis. J. Photochem.Photobio. A: Chem. 2008, **194**: 1-10.

[2] American Public Health Association (APHA), 1997. Standard Methods for the Examination of the Water and Wastewater, nineteenth edition. American Public Health Association , Washington. DC

[3] E,Dialysis., E.Diamadopoulis.,2008.Integration of Membrane Bioreactor coupled with reverse osmosis for advance treatment of municipal waste water. Journal of Desalinization :302-311

[4] A.M. Amat., A.Arques.,M.A Miranda .,Lopez ., 2005. Use of Ozone and/or UV in the treatment of effluents from Board Industry. Journal of Chemosphere:1111- 1117

[5] l.Bijan., M.Mohsouni.,2005. Integrated Ozone and bio-treatment of pulp mill effluent and change in biodegradability and molecular wt. distribution of organic compounds . Journal of Water Resources ., 39 : 3763-3772

[6] Alaton A.I., Balcioglu I.A., Bahnemann D.W., 2002. Advanced oxidation of a reactive dye bath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes. Journal of Water Resources, 36:1143

[7] Perry, C.(2011). Accounting for water use: Terminology and implications for saving water

and increasing production. *Agricultural Water Management, 98*, 1840-1846.https://doi.org/10.1016/j.agwat.2010.10.002

[8] Mavrov, V.,& Belieres, E.(2000). Reduction of water consumption and wastewater quantities in the food industry by water recycling using membrane processes. *Desalination, 131*, 75-86. https://doi.org/10.1016/S0011-9164(00)90008-0 [9]Alkhatim, H.S., Alcaina, M.I., Soriano, E., Iborra, M.I., Lora, J., Arnal, J., 1998. "PosterTreatment of whey effluents from dairy industries by nano -filtration membranes Journal of Desalination ,119 : 177-183.

[10] Azbar, N., Dokgöz, F.T.Ç, Keskin, T., Korkmaz, K.S., Syed, H.M., 2009. Continuous fermentative hydrogen production from cheese whey wastewater under thermophilic anaerobic conditions. International Journal of Hydrogen Energy, 34:7441-7447.

[11] Siso.M.I.G.,1996. The biotechnological utilization of cheese , a review. Journal of Bio resource technology,57: 1-11.

[12] Dewit.J.N., 2001. Handbook on Whey and Whey products.First edition of European Whey Products Association, Brussels: Belgium

[13] Ghaly, A.E., Singh, R.K., 1985. Land application of cheese whey. In: Proc. the 5th Intl. Symp. on Agricultural Wastes. American Society of Agricultural Engineers, Michigan, Chicago, United States of America: 546-553.

[14] Dragone.C., Mussatto.SI., Silva.J.B.A., Teixeira.JA.,2011. Optimal fermentation conditions for maximizing ethanol production by khuveromyces fragiles from cheese whey powder . Journal of Biomass Bioenergy ,35: 1977-82.

[15] Backuset, B.D., Clanton, C.J., Goodrich, P.R., Morris, H.A., 1988. Carbon-to- nitrogen ratio and hydraulic retention time effect on the anaerobic digestion of cheese whey. Trans. ASABE ,31 : 1274-1282.

[16] Ergudar,T.H.,Tezel.,Guven.E.,Demirer,G.N.,2001.Anaerobic biotransformation and methane generation potential of cheese whey in batch and UASB reactors. Waste Management.21(7):643-650

[17] Koukotas.Y., Dimitropoutou.S., Kanellaki.M., Merchant.K., Nigam.P., Banat.J.M., Koutinas.AA., 2002. High Temperature Alcoholic Fermentation of Whey using IMB 3 yeast imboloized delignified cellulose material. Journal of Bio- resource Technology ,82:177-181.

[18] Janczukowicz.W., Zielinski.M.,Debouski .M., 2008. Biodegradability Evaluation of Diary effluents originated from selected sections of Dairy production. Journal of Bio-resource technology,99: 4199-4205.

[19] Gekas.V., Lopez Leiva.M., Hydrolysis of Lactose, a literature review process. Journal of Biochem,20:2-12

[20] Guimaraes.P.MR., Francois.J.,Parrou.J.L., Yeixcira.JA., Domingues.L., 2008. Adaptive evaluation of Lactose consuming Saccharomyces cerevisiae recombinant. Journal of Applied Environmental Microbiology ,74:1748-1756

[21] Guven.G.,Perendeei.A.,Tanyolac.A.,2008. Electochemical treatment of deproteined whey wastewater and optimization of treatment condition with response surface methodology. Journal of Hazardous Matter.157(1),69-78.

[22] Jonson, H.V.,Lewis,M.J., 1994 Electrochemical coagulation of whey protein : International Journal of Diary Technology, 47(3):87-90.

[23] Glacomo.G., Di.Del.G., Spera.D., 1997. Milk Whey treatment with recovery of valuable products. Journal of Desalinization ,108: 273-276.

[24] Qureshi.N.,Manderson.G.I.,1995.Bioconversion of renewal resources into ethanol: an economic evaluation of selected hydrolysis, fermentation and membrane technologies. Energy Source 17(2).241-265

[25] Davila-Vazquez, G., Alatriste-Mondragón, F., León-Rodríguez, A., Razo-Flores, E.,2008. Fermentative hydrogen production in batch experiments using lactose,cheesewhey and glucose: influence of initial substrate concentration and pH.International Journal of Hydrogen Energy, 33 : 4989-4997.

[26] B.A Carpenttier,in ., M.R. Seventants (Ed)., 1987. Supercritical Fluid Extraction and Chromatography, (ACS Symposium Series No 366), ACS Washington, DC.

[27] Pathumthip Tonthubthimthong.,Supaporn Chuaprasert.,Peter Douglas.,Wilai Luewisutthichat., 2001. Superficial CO_2 extraction of nimbin from neem seeds-an experimental study . Journal of Food Engineering , 47(2001) 289-293 .

11. Abbreviation Used:- API (Active Pharmaceuticals Ingredient), FMCG (Fast Moving Consumer Goods, IPPC(Integrated Pollution Prevention and Control), BREF (Back Reference Documents), TOC(Total Organic Carbon), NF(Nano Filtration), BWRO (Back Water Reverse Osmosis),SFE(Supercritical Fluid Extraction), FO/RO/MD (Forward Osmosis/ Reverse Osmosis/Membrane Distillation),MBR (Membrane Bioreactor),USPEA(United State Environmental Protection Agency), ZIMI(Zero Impact Manufacturing Initiative).UV(Ultraviolet),TiO_2(Titanium Dioxide), (H_2O_2) Hydrogen Peroxide,O_3(Ozone),JIMBR(Jet Loop Membrane Bioreactor),CSTR(Continuous Flow Stirred Tank Reactor),HRT(Hydraulic Retention Time)

Annexure 1-A

Format-1 - Data Collection from Process Industry

Sl no	Name of Industry					
1	Products Manufactured KG or T/Day or Nos/Day					
2	Raw Material KG or T/Day or Nos/Day					
3	Fuel/Energy Consumption /Day					
4	Water Consumption KL/Day	Process	Cooling	Boiler	Domestic	Any other purpose/source
5	Water consumptionKL/kg of Product					
6	Waste Water Discharge KL/Day	Process		Domestic		Misc
7	Waste Water Discharge KL/kg of Product					
	Details of Chemicals with quantity kg/day					
8	Quantity of Chemicals kg/kg of product					
9	Source of Water					
10	By Product Manufactured T/Day					
11	Process Residues T/day					
12	Solid Waste T/Day					

Annexure 1-B

Format-2- Data on manufacturing details in Process Industry

S No	Details of Equipment and Machinery used in manufacturing process		
1	Type	Formulation	Bulk Drugs
	Material(Vessel, Reactor)		
2	No of Reactors		
3	No of Batches/day		
	Ingredients for composition of Batch with %age		
4	Physical parameters		
	Inlet temp ^{0}C		
	outlet temp ^{0}C		
	Pressure mm g		
5	Environmental Parameters		
	Water Consumption /batch		
	Waste Water generation/batch		
6	CIP frequency		
	Water consumption		
	Chemical used/day		
	Solvent Recovery cycle (in process		
	Solvent / By product recovery prior to ETP		
7	Energy consumption for Kg of steam and electricity in Kwh		
	Process (Steam) kg/kg of product		
	Process(Electricity) kwh/kg of Product		
	Utilities (steam in Kg/day)		
	ETP Kwh/kl of waste water treated		
	Other Misc. Details		